

Radiation-Induced Emulsion Polymerization of Tetrafluoroethylene

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Synopsis

The radiation-induced emulsion polymerization of tetrafluoroethylene was carried out with the use of ammonium perfluorooctanoate as an emulsifier at an initial pressure of ca. 30–35 kg/cm². The polymerization rate was shown to be proportional to about the 0.8 power of the dose rate in the range of 2×10^4 to 10^6 R/hr and to be almost independent of emulsifier concentration. The molecular weight of the polymer lies in the range of 10^4 to 10^5 , increases with reaction time at the initial stage, and decreases with emulsifier concentration, but is independent of the dose rate from 2×10^4 to 6×10^4 R/hr. If the emulsifier is not used, a polymer with a molecular weight as high as 1.8×10^6 to 2×10^7 is obtained. Apparently, the emulsifier and its radiolysis products act as chain transfer agents. Postirradiation polymerization was found to take place with the formation of products with increased molecular weight.

INTRODUCTION

Several studies¹⁻⁴ have been reported on the bulk and solution polymerization of tetrafluoroethylene induced by gamma radiation, whereas no paper except patents has appeared on emulsion polymerization. The molecular weights of poly(tetrafluoroethylenes) produced by radiation and conventional methods have been scarcely investigated in connection with polymerization conditions since the molecular weight measurement is difficult.

The present paper includes studies on the radiation-induced polymerization of tetrafluoroethylene in emulsion. The effects of polymerization conditions, such as agitation speed, dose rate, and emulsifier concentration, on the polymerization rate and on molecular weight are described. The molecular weight was found to increase with decreasing emulsifier concentration. Postirradiation polymerization was observed with formation of high molecular weight polymers.

EXPERIMENTAL

Tetrafluoroethylene (TFE) was provided by Mitsui Fluorochemical Co., Ltd., was stored in a cylinder under pressure with stabilizer. Before being used, TFE was passed through silica gel to remove the stabilizer. Ammo-

TABLE I
Standard Recipe for the Radiation-Induced Emulsion
Polymerization of Tetrafluoroethylene

Water	150 ml
Emulsifier (FC-143)	1.5 g (1 wt-% in water)
<i>n</i> -Hexadecane	2.0 ml
Tetrafluoroethylene	28 g
Dose rate	2.2×10^4 R/hr
Agitation speed	800 rpm
Reaction temperature	Room temp. (ca. 25°C)

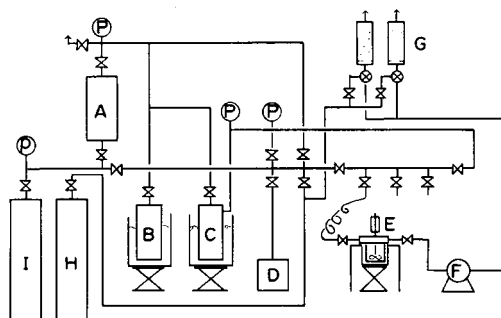


Fig. 1. Schematic diagram of experimental apparatus: A, purification column of TFE; B, C, TFE reservoir; D, vacuum pump; E, reaction vessel; F, plunger pump; G, deoxygenation vessel; H, N₂ cylinder; I, TFE cylinder; P, pressure gauge.

nium perfluorooctanoate (FC-143) and *n*-hexadecane of reagent grade were used without further purification. Twice-distilled water was used.

A schematic diagram of the experimental apparatus is shown in Figure 1. The reaction vessel was a 200-ml autoclave of stainless steel equipped with a magnetically driven agitator with a marine propeller.

The required amounts of emulsifier and *n*-hexadecane (an inhibitor for the polymerization in the gas phase) were charged in the reactor, which was then evacuated for about 10 min and swept out five times with nitrogen at 10 kg/cm² and three times with TFE at 5 kg/cm². The monomer containing the stabilizer was introduced into a purification column A at a pressure of 1 to 2 kg/cm², where the stabilizer was removed on silica gel and trapped in a vessel B at liquid nitrogen temperature. The pure TFE in vessel B was transferred to vessel C. The desired amount of TFE was fed into the reactor cooled by liquid nitrogen from vessel C maintained at 25°C. The amount of the fed monomer was determined from the pressure reduction in the vessel C. The water was flushed with nitrogen to remove oxygen and fed into the reactor by a plunger pump F. The amount of fed water was determined from the decrease in water level of vessel G. After being agitated for 30 to 60 min to obtain a stable emulsion, the reaction system was irradiated by cobalt 60 under the desired conditions. Standard experimental conditions are shown in Table I.

Poly(tetrafluoroethylene) (PTFE) obtained in latex form was isolated by freezing, washed with methanol and water, and dried under vacuum at room temperature. The molecular weight of polymer was determined from the heat of crystallization measured with a Perkin-Elmer 1B differential scanning calorimeter (DSC) by using the following relation between number-average molecular weight and the heat of crystallization⁵:

$$\bar{M}_n = 2.1 \times 10^{10} \Delta H_c^{-5.16}$$

where \bar{M}_n is the number average molecular weight and ΔH_c is the heat of crystallization, in cal/g.

RESULTS AND DISCUSSION

Effect of Agitation Speed

In order to clarify which is the rate-controlling process, polymerization reaction or monomer diffusion, the effect of agitation speed on the overall polymerization rate was examined. Figure 2 shows the relation between polymer yield and reaction time at various agitation speeds in two opposing directions. The results clearly show that the rate of polymerization is considerably affected by the rate and the direction of agitation. Figure 3 shows the mixing patterns examined in a transparent vessel of the same dimension as the reactor. The mixing of gas and liquid is improved with increasing agitation speed. Agitation which makes the flow pattern moving from the outside to the center (Fig. 3b) gives better mixing than that in the opposite direction (Fig. 3a).

These results suggest that the diffusion or dissolution of TFE into the aqueous phase is the rate-determining process under milder agitation; whereas under the agitation of Figure 3b (more than 600 rpm), the diffusion

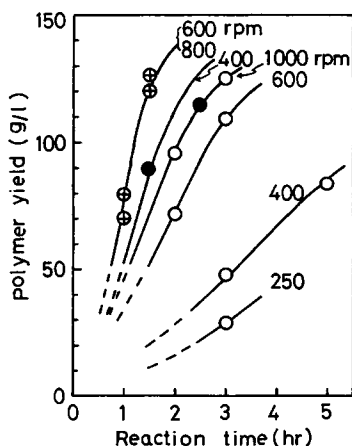


Fig. 2. Effect of agitation speed on polymer yield: (O) agitation shown in Fig. 3a was applied; (●⊕) agitation shown in Fig. 3b was applied. Reaction conditions are as shown in Table I.

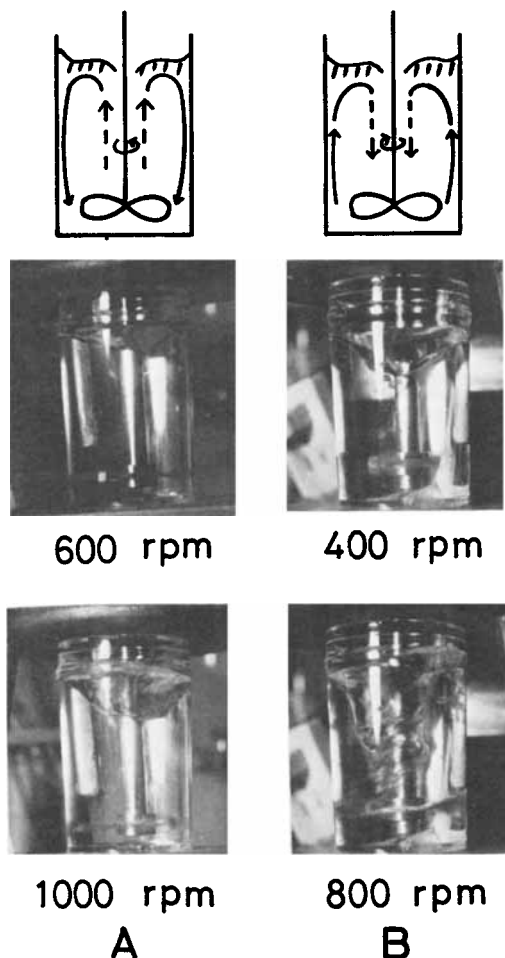


Fig. 3. Mixing patterns in a model reactor under various agitation speeds and with two different directions.

rate of TFE is larger than the rate of monomer consumption in the polymerization, so that the polymerization is the rate-determining process. Agitation at 800 rpm in this direction was applied in the following experiments.

Effect of Dose Rate

The experimental results are summarized in Table II. Figure 4 shows the relation between polymer yield and reaction time at various dose rates from 2×10^4 to 10^5 R/hr. The polymerization rates determined from the slope of the straight portion of the sigmoid curves were plotted against dose rate in Figure 5. The dose rate exponent of 0.8 found in Figure 5 is considerably larger than the 0.5 expected from kinetics assuming bimolecular termination. This discrepancy seems to be due to a small termination

TABLE II
Effect of Dose Rate on Polymer Yield and Molecular Weight^a

Run no.	Dose rate, $\times 10^{-4}$ R/hr	Reaction time, min	Pressure in reactor, kg/cm ²		Polymer yield		Conversion $X = \frac{P_0 - P}{P_0} \times 100$	Latex pH	Molecular weight $\bar{M}_n \times 10^{-4}$
			P_0	P	W , wt-%	V , g/l.			
63	2.16	60	32	17.5	7.32	79.5	45.3	—	32
67	2.16	120	34.5	5.0	10.7	120.6	85.5	—	—
90	2.16	45	32.5	28.0	1.85	19.0	13.8	4.45	12.5
91	3.66	40	32.5	24.5	4.10	43.2	24.6	4.50	—
74	3.66	50	32.5	12.5	9.64	107.7	61.5	4.50	33
80	6.00	20	33.0	22.0	6.20	67.1	33.3	4.85	16
79	6.00	30	34.0	12.0	9.98	112.0	64.7	4.45	32
75	10.2	10	34.3	19.5	7.90	86.6	43.1	4.90	24
73	10.2	20	34.2	6.5	11.0	125.4	81.0	4.95	22

^a Polymer yield shown in V , W , and X is defined as follows:

$$V = \frac{\text{polymer}}{\text{water}} \text{ (g/l.)}$$

$$W = \frac{\text{polymer}}{\text{polymer} + \text{water} + \text{emulsifier}} \times 100 \text{ (wt-\%)}$$

$$X = \frac{P_0 - P}{P_0} \times 100 \text{ (conversion \%)}$$

where P_0 and P are the pressure of the autoclave before and after the polymerization, respectively.

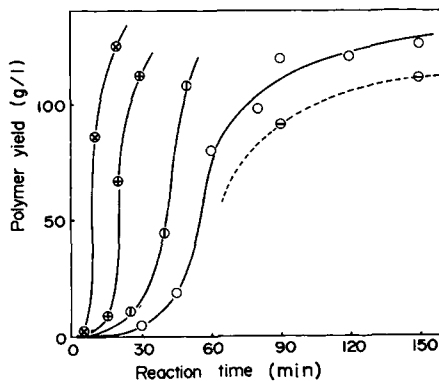


Fig. 4. Relation between polymer yield and reaction time at various dose rates: (○) 2.2×10^4 ; (⊖) 3.7×10^4 ; (⊕) 6.0×10^4 ; (⊗) 10.2×10^4 ; (⊙) 2.2×10^4 R/hr (400 rpm). Other reaction conditions are as shown in Tables I and II.

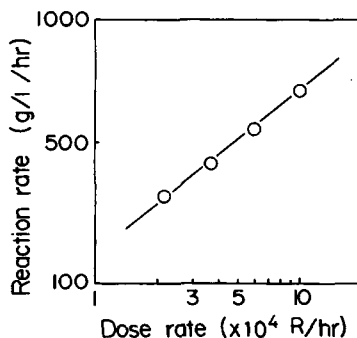


Fig. 5. Dependence of polymerization rate on dose rate. Reaction conditions are as shown in Tables I and II.

rate, which is consistent with the observation of a remarkable postirradiation polymerization. The G -values of monomer consumption for the experiments in Figure 5 ranged from 8.7×10^5 to 12.4×10^5 .

Table II indicates that the molecular weight of polymer is not greatly influenced by the dose rate.

Effect of Emulsifier Concentration

The results are shown in Table III. The rate of polymerization is shown to be scarcely affected by the emulsifier concentration above and below the critical micelle concentration (CMC). Here, the CMC of FC-143 was determined to be 0.5 wt-% from the measurement of surface tension.

The rate of emulsion polymerization of a monomer insoluble in water such as styrene is proportional to the 0.6 power of emulsifier concentration,⁶ whereas in the case of water-soluble monomer such as vinyl acetate, the rate is almost independent of emulsifier concentration.⁷ The independence of the rate from the emulsifier concentration observed in this polymerization may be associated with the fact that TFE is rather water soluble.

TABLE III
Effect of Emulsifier Concentration on Polymer Yield and Molecular Weight

Run no.	Emulsifier concentration, wt-%	Reaction time, min	Pressure in reactor, kg/cm ²		Polymer Yield		Latex pH	Molecular weight $\bar{M}_n \times 10^{-4}$
			P_0	P	W, wt-%	V, g/l.		
103	0	60	29.5	16.3	5.94	63.2	3.55	180
111	0	90	28.0	7.0	7.01	75.3	2.85	270
112 ^a	0	90	29.5	10.0	4.53	47.5	2.85	2000
101	0.2	60	29.0	16.0	5.56	59.0	4.30	120
104	0.5	60	29.6	21.5	2.88	29.8	4.50	47
106	0.5	90	30.0	15.0	4.95	52.3	4.15	62
102	1.3	60	30.0	22.0	3.41	35.7	4.35	11
98	1.3	90	31.5	20.0	7.10	77.4	—	12
99	1.6	60	29.8	19.8	5.20	55.6	—	11
107	1.6	90	31.5	16.0	6.70	72.9	4.30	13
100	2.0	60	30.5	26.0	4.85	52.1	—	10
108	2.0	90	28.0	19.5	42.7	45.5	—	—

^a Polymerization at 70°C.

The morphology and molecular weight of polymer formed are markedly affected by the emulsifier concentration. The morphologies of polymers in latex observed by an electron microscope are spherical at an emulsifier concentration below 0.5 wt-%, spherical and rod-like at 0.5–1.0 wt-%, and fibrillar above 1.5 wt-%.⁸ The molecular weight increases with decrease in emulsifier concentration. The details will be described later.

The decrease of pH observed during polymerization may be due to the formation of hydrogen fluoride by radiolysis of TFE in water. The fact that the decrease of pH is less remarkable in the presence of the emulsifier is probably ascribed to the adsorption of hydrogen fluoride by the emulsifier (ammonium perfluorooctanoate).

Postirradiation Polymerization

Postirradiation polymerization of TFE was reported to occur in bulk and in solution.⁴ As shown in Figure 6 and Table IV, postpolymerization was

TABLE IV
Results of Postirradiation Polymerization

Run no.	In-source polymerization				Postpolymerization			
	Dose rate, $\times 10^{-5}$ R/hr	Irradiation time, min	Polymer yield, g/l.	Molecular weight \bar{M} $\times 10^{-4}$	Pressure in reactor, kg/cm ²		Polymer yield, g/l.	Molecular weight $\bar{M}_n \times 10^{-4}$
					P_0	P		
55	1.02	15	72.0	22	14.5	4.5	106	—
57 ^a	3.00	15	89.0	—	15.5	5.0	166	64
76 ^a	1.02	10	86.6	24	20.0	18.5	189	150

^a TFE was supplied to the reactor during the postpolymerization.

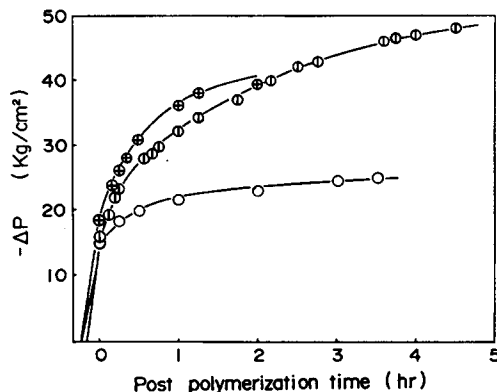


Fig. 6. Postirradiation polymerization, where ΔP is pressure reduction caused by consumption of TFE in postpolymerization: (○) preirradiation dose 2.5×10^4 R, run no. 55 in Table IV; (⊙) 1.7×10^4 R, run no. 76; (⊕) 7.5×10^4 R, run no. 57.

found also in the emulsion system. At the beginning, the rate of post-polymerization is the same as in-source polymerization, and it decreases gradually with time because of chain termination. The propagating radical has a long life and continues to grow after irradiation to give a very high molecular weight polymer.

Molecular Weight of PTFE

The molecular weight of PTFE has only rarely been investigated in connection with reaction conditions because of the difficulties of the measurement. In a previous paper,⁵ we have proposed a simple and reliable method to determine the molecular weight of PTFE, which was used in this paper.

Figure 7 shows the relation between polymer molecular weight and reaction time at various dose rates. The molecular weight increases with the time at the initial stage and decrease at a later stage. The increase as reaction proceeds is due to the low termination rate bringing about successive

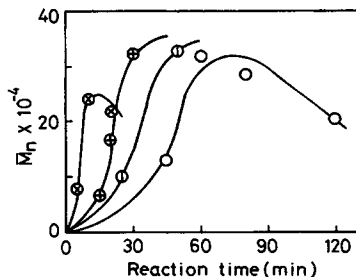


Fig. 7. Relation between molecular weight of polymer and reaction time at various dose rate: (○) 2.2×10^4 ; (⊙) 3.7×10^4 ; (⊕) 6.0×10^4 ; (⊗) 10.2×10^4 R/hr. Other reaction conditions are as shown in Tables I and II.

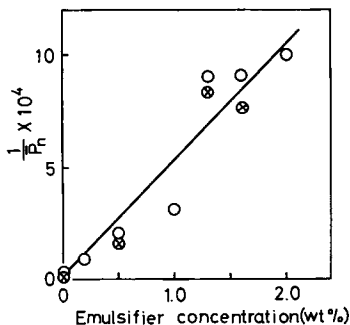


Fig. 8. Reciprocal of degree of polymerization vs. emulsifier concentration: dose rate, 2.2×10^4 R/hr; reaction time (○) 60 min, (⊗) 90 min. Other reaction conditions are as shown in Tables I and III.

chain growth; and the decrease at later stages is ascribed to the pressure reduction caused by monomer consumption.

Molecular weight was found to decrease remarkably with emulsifier concentration, as shown in Table III. Figure 8 shows the plot of the reciprocal of the degree of polymerization against emulsifier concentration. In the in-source polymerization with emulsifier, very high molecular weight polymer is not obtained; whereas the conventional emulsion polymerization using radical initiator gives very high molecular weight polymer, even in the presence of emulsifier. These facts indicate that the radiolysis products of the emulsifier act as chain transfer agents.

Extremely large molecular weight polymers, such as \bar{M}_n of 2×10^7 and 3×10^6 , are found to be formed in latex when the emulsifier is not used. A detailed study of suspension polymerization without using emulsifier is in progress.

Melting Point and Heat of Fusion of PTFE

Melting point and heat of fusion of virgin PTFE are summarized in Table V. The melting point is around 330°C for the polymer with molecular weight lower than 10^6 , and it increases with molecular weight higher than 10^6 . The heat of fusion was about 13 cal/g, which is nearly the same as that of commercial PTFE.⁹

Polymerization Mechanism

According to the Harkins' hypothesis,¹⁰ polymer particles are generated principally in micelles swollen with solubilized monomer. The reaction theoretically starts when a free radical from the aqueous phase invades a swollen micelle and activates a solubilized monomer molecule. Chain growth follows at the expense of solubilized monomer until it is terminated with another similarly produced radical chain in the same micelle.

The Harkins' hypothesis does not seem to be applicable to this polymerization system, because the rate of polymerization is almost independent of

TABLE V
 Melting Point and Heat of Fusion of PTFE

Run no.	$\bar{M}_n \times 10^{-4}$	$T_m, ^\circ\text{C}$	$T_c, ^\circ\text{C}$	$\Delta H_f, \text{cal/g}$
90	12.5	329	307	12.7
63	32	332	307	13.6
74	33	333	309	12.3
73	22	332	308	12.8
79	32	328	306	13.4
57	64	331-336	308	12.8
76	150	331-338	307	13.4
111	270	331	307	13.2
112	2000	338-344	308	12.6
EP ^a	960	337-342	308	13.3
SP ^b	4500	344	310	11.9

^a Commercial PTFE prepared by emulsion polymerization.

^b Commercial PTFE prepared by suspension polymerization.

 TABLE VI
 Number of Polymer Chains Formed at Various Emulsifier Concentrations^a

Run no.	Emulsifier concn., wt-%	No. of polymer chains, $10^{16}/\text{ml}$
103	0	2.11
101	0.2	2.97
104	0.5	3.82
63	1.0	15.0
102	1.3	19.6
99	1.6	30.4
100	2.0	31.4

^a Polymerization conditions: dose rate, $2.16 \times 10^4 \text{R/hr}$; reaction time, 60 min.

the emulsifier concentration. Moreover, the morphology of latex changes in a complicate manner with varying emulsifier concentration. In this system, there are presumably two loci for chain initiation leading to the generation of polymer particles, namely, the monomer solubilized in micelle and the monomer dissolved in the aqueous phase. As mentioned above, since the rate of polymerization is almost independent of the emulsifier concentration, the later locus appears to play a more important role than the former. It is assumed that the polymer generation starts mainly from the aqueous phase and the emulsifier in forming the micelle is gradually adsorbed on the polymer-water interface to make the polymer latex.

The number of polymer chains was calculated by dividing the polymer yield by the molecular weight as shown in Table VI. It is considered that an initiating radical is produced mainly by the radiolysis of water, since the amount of water is much larger than that of TFE. The G -value of radical formation from water has been reported as follows:¹¹⁻¹²

$$G = G_{\text{OH}} + G_{\text{H}} + G_{\text{e}_{\text{aq}}^-} = 2.2 + 0.5 + 2.8 = 5.5$$

and the total number of radicals formed in 1 hr was calculated as $7.23 \times 10^{16}/\text{ml}$ at a dose rate of $2.16 \times 10^4 \text{R/hr}$. Interestingly, the number of

polymer chains well coincides with the calculated number of initiating radicals in order of magnitude. This indicates that the above assumption, that is to say, that initiating radicals are formed mainly from water, is reasonable.

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